The dark side of DFT based transport calculations

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We compare the conductance of an interacting ring of six lattice sites threaded by flux π in a two terminal setup with the conductance of the corresponding Kohn-Sham particles. Based on symmetry considerations we can show that even within (lattice) Density Functional Theory employing the exact Functional the conductance of the Kohn-Sham particles is exactly zero, while the conductance of the physical system is close to the unitary limit. We show that this fundamental problem might be solved by extending the standard DFT scheme.

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Running an electrical current through individual molecules and being able to control the current flow by molecular design is one of the intriguing aspects of Molecular Electronics. In order to model the transport properties of a molecule one has to take the contact region into account. Leading to the problem of many degrees of freedom. The "standard method" is a combination of Kohn-Sham (KS) density functional theory (DFT) calculations and the (self consistent) Landauer approach. [1–3] At least for larger molecules, comprising a few hundred electrons, the standard approach appears to be without computationally feasible alternative, at present. Recently, the question to which extend this approach is actually justified got increased attention. At least for the the linear conductance, which can be obtained from a ground state correlation function [4, 5], one can hope that there exists a one to one mapping between the wave function and the conductance, from which a functional for the conductance would result by virtue of the Hohenberg-Kohn theorem [6]. However, the nature of such a functional is not known and there is no reason that this functional should coincide with the conductance of the Kohn-Sham auxiliary particles.

In [7] we studied the conductance of a linear chain of five strongly interacting sites via the density matrix renormalization group method [8, 9], where the conductance was obtained from the Kubo formula [4, 5]. By reverse engineering the Kohn-Sham potentials [7, 10, 11] leading to the same local densities as in the DMRG we could compare the conductance of the Kohn-Sham system with the conductance of the physical system and found an excellent agreement close to the resonances with larger deviations in the conductance valleys.[7] The agreement could be traced back to the existence of an at least approximate Friedel sum rule, where the conductance is basically given by $G = G_0 \sin^2(\pi N_{\mathrm{Dot}})$, where G_0 is the on-resonance conductance. The role of the Friedel sum rule was recently also studied in [12–15] in the context of the single impurity Anderson model, where it holds exactly.[16] Therefore, it provides a conductance functional[17], and since it also holds in the non-interacting case, the conductance of Kohn-Sham particles obtained via the Landauer approach agrees with the physical conductance. Remarkably, the spectral function can be arbitrarily wrong, despite an exact agreement between the physical and the Kohn-Sham conductance.[15] However, one should keep in mind that this is only valid within exact DFT. It was shown in [18] that evaluating the conductance within approximate functionals for the the above mentioned five site system can lead to parametrically wrong results, see also [19].

Here we compare the conductance of a hexagonal ring structure with the Kohn-Sham conductance obtained via exact DFT for a system, where the conductance is not given by a simple Friedel sum rule. To this end we look at a six site ring of spinless fermions which is threaded by a half magnetic flux quantum. The Hamiltonian of the structure is given by

$$\begin{aligned}\mathcal{H}_{\mathrm{Dot}} = &-J\sum_{x=2}^{6}\left(\hat{c}_x^+\hat{c}_{x-1}+\hat{c}_{x-1}^+\hat{c}_x\right)+J\left(\hat{c}_1^+\hat{c}_6+\hat{c}_6^+\hat{c}_1\right)\\ &+U\sum_{x=2}^{6}\left(\hat{n}_x-\frac{1}{2}\right)\left(\hat{n}_{x-1}-\frac{1}{2}\right)\\ &+U\left(\hat{n}_1-\frac{1}{2}\right)\left(\hat{n}_6-\frac{1}{2}\right)\end{aligned} \tag{1}$$

where J is the nearest neighbour hopping of the ring, U is the nearest neighbour interaction and the flux π is modeled by changing the sign of the hopping element of the 1–6 bond. The system is coupled via an hybridization of J' from site 1 to a left and from site 4 to a right lead. We are using exactly the same lead structure as in [20] where each lead starts with three real space sites and is then coupled to 34 sites represented in momentum space employing a logarithmic discretization plus a linear discretization scheme close to the Fermi surface, leading to a level spacing of the leads at zero energy of $7.6\cdot10^{-5}J$, for details see [5, 20]. The leads correspond to tight binding chains with hopping elements of J. In the DMRG we kept 1000 states per block. In order to avoid getting stuck into excited states we first performed an ini-

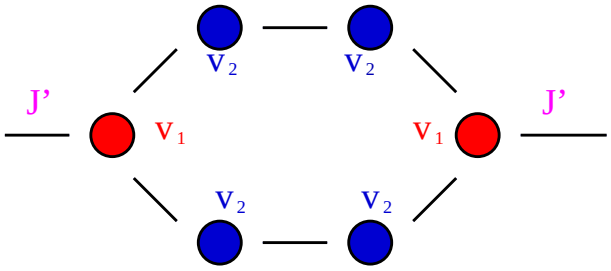

FIG. 1: (Color online) The most general set of parameter allowed by the symmetry of the system. v_1 and v_2 are the Kohn-Sham potentials of the system including the external gate voltage $V_{\rm Gate}$.

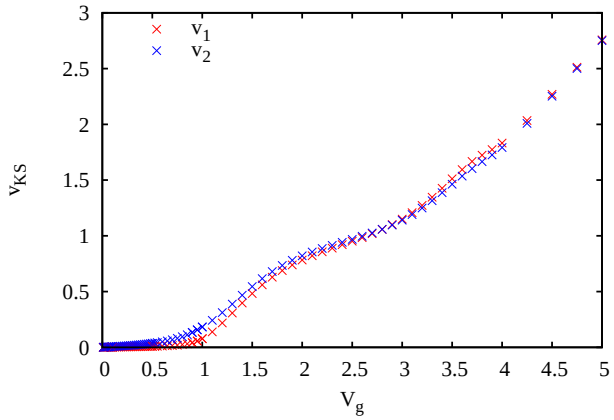

FIG. 2: (Color online) Kohn-Sham potentials v_1 and v_2 obtained by reverse engineering the solution provided by DMRG calculations. The deviations, i.e. the asymmetric parts, are of the order of $10^{-7}J$ and below.

tial run for $U = 0$ and $V_{\rm Gate} = 0$. We then restarted the DMRG increasing first the interaction U in five steps to $U = 2.25J$. Then we increased $V_{\rm Gate}$ performing 9 finite lattice sweeps for each gate voltage shown in Figure 2.

This system has the interesting property that in the noninteracting limit its linear conductance is precisely zero for all applied gate voltages $V_{\rm Gate}$ [20],

$$\hat{V}_{\rm Gate} = V_{\rm Gate} \sum_{x=1}^{6} \hat{n}_x \, . \qquad (2)$$

In contrast, a nearest neighbour interaction of the order of $U = 2t$ results in a geometric Kondo effect leading to a conductance up to approximately 0.8 e^2/h, close to the unitary limit [20]. Due to the particle hole symmetric form of the interaction U in Eq. (1) each site is exactly half filled for $V_{\rm Gate} = 0$ for any value of U. Since the conductance changes with respect to the interaction, while the densities remain constant, the conductance is not given by a Friedel sum rule. Indeed, there is no reason why such a formula should exist, since the Friedel sum rule is a statement about the spectral function, which in general has no simple relation to the conductance except for proportional coupling, e.g. isolated levels.[21]

In Figure 1 we display the most general structure of Kohn-Sham potentials that is consistent with the symmetry of the structure. That is, the potentials of the contact sites have to be identical due to inversion symmetry, and the middle four sites are subject to the same potential due to inversion and mirror symmetries of the ring structure, leading to two Kohn-Sham potentials $v_{1,2}$ only. In Figure 2 we show the reverse engineered Kohn-Sham potentials for a sample system with $J' = 0.5J$. In the low gate voltage we see a compensation of the gate voltage corresponding to the conductance plateau in the Kondo regime. For gate voltages of the order of $U/2$ we see a cross over to a Hartree regime, which gets itself interrupted by the appearance of the next pair of degenerate states. In the numerics we calculated the Kohn-Sham potentials on all real space sites, and the deviation from the symmetry as displayed in the Figure 1 are of the order of 10^{-7}, which is in agreement with the numerical accuracy. By the explicit calculation of the Kohn-Sham potentials we can show that out system is indeed v-representable, which means that a corresponding Kohn-Sham system does indeed exist. In addition we do get Kohn-Sham potentials on the lead sites. However, they only lead to a slight change of the lead Greens function.

However, it is straightforward to show, that even for arbitrary potentials v_1 and v_2 the transmission amplitude is still zero. Therefore, no matter what the actual values of the Kohn-Sham potentials are, the conductance of the Kohn-Sham auxiliary system is always zero. And since it is always zero, it doesn't matter that the lead Greens functions is changed by Kohn-Sham potentials induced in the noninteracting leads, as there are no conductance peaks which could be shifted or modified. Finally, even the introduction of an an exchange correlation voltage, as a consequence of non-adiabatic dynamic correlations stemming from the zero frequency limit of time-dependent DFT, [22] will not lead to a finite conductance, at least as long as the effective potentials are finite.

One may think that the above result is due to some extreme fine tuning of the model. We therefore introduce Kohn-Sham hopping elements in such a way, that the kinetic energy of bonds of the ring in the physical system and the auxiliary free fermion system are the same. Again, the symmetry of the ring restricts the possible hopping elements to J_1 and J_2 as displayed in Figure 3, and we can even allow for the adaption of the contact term J'. Remarkably, even with this general set of parameter, the conductance of the auxiliary system is exactly zero for all gate voltages.

In the preceding part we have shown an example where the conductance of the Kohn-Sham particles fails to de-

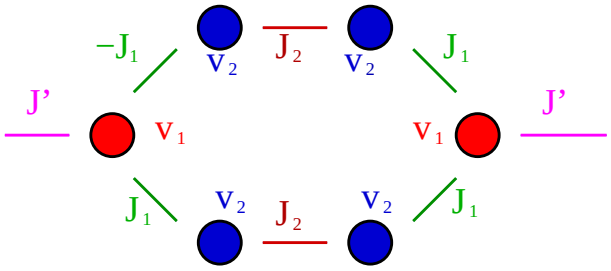

FIG. 3: (Color online) The most general set of parameter allowed by the symmetry of an extended DFT, where one also adapts the kinetic part of the Hamiltonian.

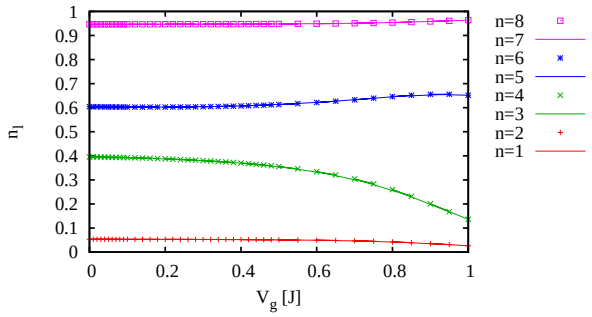

FIG. 4: (Color online) The occupation n_ℓ of the natural orbital, where for the six site structure enhanced by the first lead site of each lead. The pluses (crosses, starts, boxes) correspond to level $\ell = 2$ (4,6,8), where the lines correspond the to the degenerate partner $\ell = 1$ (3,5,7).

scribe the real physical system. In the following we want to show that the single particle description can be improved by considering a reduced single particle density matrix description. To this end we perform a ground state DMRG calculation where we extract the single particle reduced density matrix

$$K_{x,y} = \langle \Psi_0 | \hat{c}_x^+ \hat{c}_y | \Psi_0 \rangle \,, \tag{3}$$

where we restrict the site indexes to the structure and possibly including up to the first three sites of the leads closest to the structure. The results presented below are obtained from DMRG calulations where we restricted each lead to 22 levels in the momentum space description, in contrast to the 34 levels used in the reference calculation [20]. By diagonalizing K,

$$\tilde{K}_{\ell,\ell'} = f_\ell \, \delta_{\ell,\ell'} = \mathcal{U}^+ \cdot K \cdot \mathcal{U} \tag{4}$$

we obtain the occupation number f_ℓ of the so called natural orbitals given by the transformation matrix $\mathcal{U}$. In a next step we make the assumption that we can treat the natural orbitals as independent levels. Note, that due to the symmetry of our structure we still get occupation numbers in degenerate pairs, and we can still have interference effects.

The occupation numbers in the case of restricting K to the structure enhanced by the first lead site of each lead are displayed in Figure 4. In contrast to the total dot occupation which is close to an integer, $N_{\rm Dot} = 3$, we now have four levels which are close to a half integer occupation and which can contribute of transmission. Interestingly, there is an increase of the occupation of the four higher occupied levels despite the fact that we are pushing particle out of the structure by applying the gate voltage $V_{\rm Gate}$. It seems natural to blindly add the conductances of each level obtained by assuming a Friedel sum rule contribution for each level. However, due to the one-dimensional character of our leads, the complete conductance must not exceed e^2/h. We therefore weight the individual contribution with a factor w_ℓ,

$$G = \sum_\ell w_\ell \sin^2 \left(f_\ell \pi \right) \,, \tag{5}$$

where w_ℓ is set to the average occupation of the left- and right-most site of the structure under consideration, $w_\ell = \left(\mathcal{U}_{1,\ell}^2 + \mathcal{U}_{M_{\rm S},\ell}^2 \right) /2$, where $M_{\rm S}$ is number of sites of the structure plus the added real space lead sites. We would like to stress that we are not claiming that Eq. (5) combined with our choice of w_ℓ has to be a justified procedure. It is only meant to provide a first impression and to ensure that G is within the limits of zero and one conductance quantum. Using $w_\ell = \mathcal{U}_{1,\ell}^2$ or $w_\ell = \mathcal{U}_{M_{\rm S},\ell}^2$ leads to basically the same result.

In Figure 5 we compare the result of Eq. (5) applied to the six site structures, and the cases where we include one or three sites from each lead, to the Kubo result within DMRG [20]. Remarkably, in contrast to the failure of the plain DFT approach our simple approach of Eq. (5) not only gives a peak at all, it already provides the correct order of magnitude for the peak height and the peak width. We would like to stress that within this description we are beyond a single slater determinant description. Due to the non-integer occupation numbers we have actually moved to a multi reference description.

From this we conjecture that by going beyond a standard DFT description towards a reduced density matrix functional theory [23, 24] or a generalized td-CDFT [25] one should be able to improve todays simulations within molecular electronics. In summary we have provided an example where the conductance of the Kohn-Sham auxiliary particles fails remarkably to describe the physical conductance. The Kohn-Sham conductance is strictly zero for all gate voltages, while the conductance of the physical system displays resonance peaks close to the unitary limit. In contrast, by considering a description based on the eigenstates of a single particle reduced density matrix we can obtain results which are at least in the correct order of magnitude. Results presented in this work and the population blocking mechanism [20] lead to the conclusion that one should apply multi reference methods in

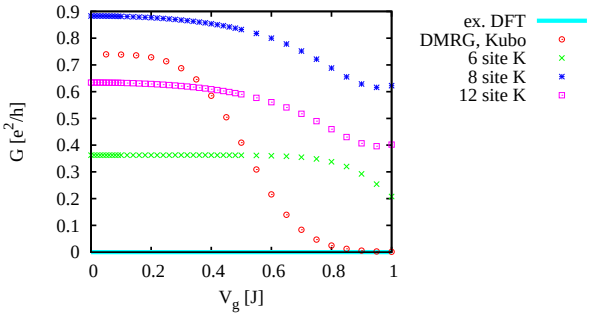

FIG. 5: (Color online) Comparison of the conductance obtained via the Kubo formalism within DMRG (circles), and the one obtained from Eq. (5), where the reduced density matrix K was restricted to the six site structure (green crosses), the structure plus the contact site of each lead (blue stars), and the structures plus the first three sites of the leads on each site (magenta squares).

order to describe transport properties interacting quantum system in the presence of interference effects within a single particle description reliably. Our finding suggest that a reduced single particle density matrix based approach is a promising candidate to study transport within a mean field type method, i.e. a single particle, description.

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